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DESCRIPTION

POLYMER ELECTROLYTE

AND NONAQUEOUS BATTERY CONTAINING THE SAME

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[TECHNICAL FIELD]

The present invention relates to a nonaqueous battery, particularly a lithium ion battery, and a nonaqueous battery containing the electrolyte.

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[BACKGROUND ART]

The development of electronic technology in recent years is remarkable, and various apparatus and devices have been reduced in size and weight.

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Accompanying the reduction in size and weight of such electronic apparatus and devices, there has been a remarkably increasing demand for reduction in size and weight of a battery as a power supply for such electronic apparatus and devices. As a battery

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capable of providing a large energy at small volume and weight, a nonaqueous secondary battery using lithium has been used as a power source for principally small-sized electronic appliances, such as portable telephone sets, personal computers and video cam coders, used at home. For the purpose of providing the lithium nonaqueous secondary battery with increased shape latitude, e.g., formation into a

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very small thickness on the order of 0.5 mm, extensive development work has been made on polymer electrolyte batteries.

A polymer electrolyte containing no  
5 electrolytic solution hardly satisfies properties required for application to batteries because of, e.g., low ionic conductivity and small battery discharge capacity. In contrast thereto, a polymer gel electrolyte containing electrolytic solution has  
10 called an attention because of a high ionic conductivity. As such a polymer electrolyte, U.S. Patent No. 5,296,318 has reported a polymer electrolyte using a copolymer of vinylidene fluoride with 8 to 25 wt. % of hexafluoropropylene. Further,  
15 as a technique for impregnating the copolymer with an increased amount of electrolytic solution, U.S. Patent No. 5,456,000 has disclosed a technique of mixing the copolymer with a plasticizer, then extracting the plasticizer and then effecting the impregnation with a  
20 nonaqueous electrolytic solution. According to this technique, it is possible to effect the impregnation with a large amount of electrolytic solution, but such impregnation with a large amount of electrolytic solution is accompanied with a problem of losing a  
25 shape latitude, such as the formation into a very small thickness. Further, as the technique essentially involves a step of extracting the

plasticizer, the productivity becomes inferior.

Further, complete extraction of a plasticizer is difficult, and a portion of the plasticizer remaining in the polymer electrolyte is liable to exert an adverse effect to the battery prepared by using the electrolyte.

In order to obtain a polymer electrolyte battery having a high shape latitude, it is essential to provide a polymer gel electrolyte capable of containing a large amount of electrolytic solution so as to enhance the ionic conductivity and yet exhibiting a large strength. However, the strength of a gel is lowered at a larger content of electrolytic solution, so that it has been impossible to satisfy a gel strength and a content of electrolytic solution in combination, and no polymer gel electrolyte suitable for providing a polymer electrolyte battery having a high shape latitude has been known.

In order to increase the gel strength, it is considered important to provide an enhanced modulus of elasticity to the gel. Factors controlling the elasticity modulus of a gel have been generally obscure except that a higher polymer concentration provides a higher elasticity modulus (but this results in a lower content of electrolytic solution in the polymer electrolyte and is thus not practical), and it has been reported that an increase in polymer

molecular weight does not result in a change in elasticity modulus with respect to  $\kappa$  carrageenans gel by Rochas, C. et al, Carbohydrate Polymers, 12, 255 - 266 (1990). In this way, as general guiding principles for enhancing the gel strength, none have been known except for relying on a higher polymer concentration. Accordingly, a practical polymer electrolyte capable of being impregnated with a large amount of nonaqueous electrolytic solution and yet having an excellent strength, has not been known.

Further, in the case of being impregnated with a large amount of nonaqueous electrolytic solution, it is necessary to stably retain the solution and prevent the solution from leaking out of the polymer electrolyte. If the nonaqueous electrolytic solution cannot be stably retained and a large amount of leakage thereof is caused, it becomes impossible to obviate damages and deterioration of electrical properties of apparatus and devices surrounding the battery.

#### [DISCLOSURE OF INVENTION]

The present invention aims at providing a polymer electrolyte capable of being impregnated with a large amount of nonaqueous electrolytic solution and stably retaining the electrolytic solution and yet exhibiting excellent strength, and further a

nonaqueous battery having a large shape latitude by using the polymer electrolyte.

According to the inventors' study for accomplishing the above objects, it has been found very preferable to use a polymer electrolyte, comprising: a vinylidene fluoride copolymer and a nonaqueous electrolytic solution, wherein the vinylidene fluoride copolymer comprises 80 to 97 wt. % of vinylidene fluoride monomer units and 3 to 20 wt. % of units of at least one monomer copolymerizable with vinylidene fluoride monomer and has an inherent viscosity of 1.5 to 10 dl/g. Herein, "inherent viscosity" is used as a measure of polymer molecular weight and refers to a logarithmic viscosity number as measured at 30 °C of a solution formed by dissolving 4 g of a polymer resin in 1 liter of N,N-dimethylformamide.

#### [BRIEF DESCRIPTION OF THE DRAWINGS]

Figure 1 is a sectional view in a thickness-wise direction of a nonaqueous battery using a polymer electrolyte according to the present invention.

#### [EMBODIMENTS OF THE INVENTION]

The polymer electrolyte according to the present invention comprises a vinylidene fluoride copolymer and a nonaqueous electrolytic solution,

wherein the vinylidene fluoride copolymer comprises 80 to 97 wt. % of vinylidene fluoride monomer units and 3 to 20 wt. % of units of one or plural species of monomer copolymerizable with vinylidene fluoride  
5 monomer and has an inherent viscosity of 1.5 to 10 dl/g, preferably 1.7 to 7 dl/g.

As a polymer matrix capable of keeping electrochemical stability while containing an electrolytic solution in a lithium nonaqueous  
10 secondary battery, it is possible to suitably use, e.g., a vinylidene fluoride-hexafluoropropylene or a vinylidene fluoride-trifluorochloroethylene copolymer. If the content of the monomer other than vinylidene fluoride is below 3 wt. %, the content of the  
15 electrolytic solution cannot be increased, and if the vinylidene fluoride monomer content is below 80 wt. %, the liquid-retentivity of the polymer electrolyte is lowered in the case of retaining a large amount of electrolytic solution, thus being liable to cause the  
20 exudation of the electrolytic solution, so that the vinylidene fluoride monomer unit content should be in the range of 80 wt. % to 97 wt. %. A ternary copolymer comprising hexafluoropropylene and trifluorochloroethylene in a total amount of 3 - 20  
25 wt. % in addition to 80 - 97 wt. % of vinylidene fluoride, may also be preferably used.

The vinylidene copolymer may be produced

through a process, such as suspension polymerization, emulsion polymerization or solution polymerization, and the polymerization process need not be particularly restricted. For the purpose of, e.g.,

5 improving the properties of the resultant polymer electrolyte, it is possible to adjust a method of adding copolymerizable monomers, a polymerization temperature, etc. As for the method of adding copolymerizable monomers, e.g., in the case of

10 copolymerization of vinylidene fluoride and hexafluoropropylene, the polymerization of vinylidene fluoride and hexafluoropropylene charged simultaneously can provide a polymer resulting in a polymer electrolyte capable of exhibiting a higher

15 strength and a higher liquid-retentivity and is therefore advantageous than in the case of polymerization of vinylidene fluoride and hexafluoropropylene charged in division or continuously. As for the polymerization temperature,

20 a higher temperature provides a polymer resulting in a polymer electrolyte exhibiting a higher liquid-retentivity and is therefore advantageous. A temperature of 25 °C or higher is generally suitable. In the case of suspension polymerization, for example,

25 a temperature of 25 °C - 50 °C is suitable at the initial stage but it is also preferred to raise the temperature up to ca. 80 °C at a later stage.

Further, in the case of emulsion polymerization, it is possible to raise the temperature up to ca. 150 °C from the initial stage.

5 A vinylidene fluoride copolymer of a high liquid-retentivity obtained by such a relatively high polymerization temperature is characterized by an increase in abnormal linkage or different-type linkage (head-head or tail-tail linkage) at vinylidene fluoride sites formed of successive or adjacent  
10 vinylidene fluoride polymerized units as confirmed by NMR. Such an abnormal linkage content should preferably be at least 3 % of vinylidene fluoride sites.

Incidentally, U.S. Patent No. 5,296,318 has  
15 disclosed the use of a vinylidene fluoride copolymer having a relatively low vinylidene fluoride monomer unit content by including 8 - 25 wt. % of hexafluoropropylene so as to provide an increased impregnation content of nonaqueous electrolytic  
20 solution. In the present invention, however, even at a higher vinylidene fluoride content of, e.g., 93 wt. %, a high impregnation content of nonaqueous electrolytic solution can be attained together with a remarkably improved retentivity of non-aqueous  
25 electrolytic solution (see Examples 1, 4, etc., described later). While the reason therefor is not clear as yet, the effect is understood as an effect



accompanying an increased inherent viscosity of at least 1.5 dl/g, i.e., an increased molecular weight, of the copolymer (see Examples and Comparative Examples described later).

5           If the polymer has an inherent viscosity of below 1.5 dl/g, the resultant polymer electrolyte is caused to have a weak strength at a high electrolytic solution content region usable as a battery, and a short circuit between the positive and negative  
10 electrodes is caused when a thin battery is formed and folded, so that the polymer electrolyte is difficult to use from a viewpoint of dynamical strength. There is observed a tendency that a higher inherent viscosity of polymer results in a polymer electrolyte  
15 exhibiting a higher strength, but above a certain inherent viscosity, the strength tends to be saturated. Moreover, an inherent viscosity in excess of 10 dl/g results in a problem in respect of productivity of the vinylidene fluoride that it  
20 becomes difficult to form a thick solution thereof in a volatile solvent.

More specifically, a vinylidene fluoride copolymer comprising 80 - 97 wt. % of vinylidene fluoride monomer units and 3 - 20 wt. % of one or  
25 plural species of monomer copolymerizable with vinylidene fluoride and having an inherent viscosity of 1.5 - 10 dl/g, allows easy formation of a gel film,

which shows a good liquid-retentivity and a large film strength even in a gel state containing an electrolytic solution in an amount as large as 300 wt. % of the polymer (i.e., an electrolytic solution content in the gel of 75 wt. %), so that it is suitably used in a nonaqueous battery comprising a polymer electrolyte. The polymer electrolyte according to the present invention can be used in a state of containing an electrolytic solution at a large content of ordinarily 50 wt. % to 85 wt. %.

There is observed a tendency that a polymer electrolyte exhibits a higher lithium ionic conductivity at a higher electrolytic solution content. For example, the above-mentioned U.S. Patent No. 5,296,318 discloses that gels having electrolytic solution contents in the range of 20 wt. % - 70 wt. %, substantially 40 - 60 wt. %, show lithium ion conductivities ranging from  $10^{-5}$  S/cm to  $10^{-3}$  S/cm. Accordingly, it is ensured that the polymer electrolyte gel according to the present invention capable of exhibiting a higher electrolytic solution content of 50 - 85 wt. % in the polymer electrolyte exhibits a level of ionic conductivity sufficient for function as an actual battery material. Particularly, the polymer electrolyte according to the present invention shows a sufficient gel strength in a state of containing an electrolytic solution in a proportion

as high as 85 wt. % as shown in Examples described later.

Examples of the monomer copolymerizable with vinylidene fluoride monomer may include: hydrocarbon monomers, such as ethylene and propylene; fluorine-containing monomers, such as vinyl fluoride, trifluoroethylene, trifluorochloroethylene, tetrafluoroethylene, hexafluoropropylene, and fluoroalkyl vinyl ether; carboxyl group-containing monomers, such as monomethyl maleate and monomethyl citraconate; and epoxy group-containing vinyl monomers, such as ally glycidyl ether and glycidyl crotonate, but these are not restrictive. It is however preferred to use vinylidene fluoride copolymers containing hexafluoropropylene and/or trifluoroethylene among the above.

The nonaqueous electrolytic solution constituting the gel-form polymer electrolyte according to the present invention together with a matrix of the above-mentioned vinylidene fluoride copolymer may, for example, be obtained by dissolving an electrolyte, such as a lithium salt, in a proportion of 5 - 30 wt. parts in 100 wt. parts of a nonaqueous solvent (organic solvent).

The electrolytes may for example include:  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiCl}$ ,  $\text{LiBr}$ ,  $\text{LiCH}_3\text{SO}_3$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  and  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ . The organic

solvent for the electrolyte may for example include:  
propylene carbonate, ethylene carbonate, 1,2-  
diethoxyethane, 1,2-diethoxyethane, dimethyl  
carbonate, methyl ethyl carbonate,  $\gamma$ -butyrolactone,  
5 methyl propionate, ethyl propionate, and solvent  
mixtures of these, but these are not restrictive.

The polymer electrolyte according to the  
present invention may be formed from the above-  
mentioned vinylidene fluoride copolymer resin (or a  
10 mixture thereof with another resin) and nonaqueous  
electrolytic solution, e.g., in the following manner.  
First, an electrolyte is dissolved in an organic  
solvent to form an electrolytic solution in a manner  
as described above. Then, a vinylidene fluoride  
15 resin is dissolved in a volatile organic solvent to  
form a solution, which is blended with the above  
nonaqueous electrolytic solution. Further, via a step  
of vaporizing the above-mentioned volatile organic  
solvent, a polymer electrolyte in the form of a film  
20 is obtained. The volatile organic solvent used in  
this instance may preferably be one which is readily  
volatile by having a high vapor pressure at a  
relatively low temperature and can well dissolve the  
vinylidene fluoride copolymer. Tetrahydrofuran,  
25 methyltetrahydrofuran, acetone, methyl ethyl ketone,  
1,3-dioxalan, cyclohexanone, etc., may be used, but  
these are not restrictive.

Further, propylene carbonate, ethylene carbonate, dimethyl carbonate, etc., frequently used as an organic solvent for dissolving an electrolyte can per se be used as a solvent for the vinylidene fluoride copolymer, so that it is possible to form a polymer electrolyte without using a volatile organic solvent as described above. In this instance, it is possible to first dissolve a vinylidene fluoride copolymer in an organic solvent to form a solution and then add an electrolyte thereto for further dissolution, or to dissolve a vinylidene fluoride copolymer and an electrolyte simultaneously in an organic solvent. The resultant solution containing the vinylidene fluoride copolymer and the electrolyte is cooled to room temperature for gelation, thereby forming a film structure comprising a polymer electrolyte in the form of a film.

A basic structure of a nonaqueous battery using a polymer electrolyte according to the present invention may be obtained as shown in a sectional view of Figure 1 by disposing a generally sheet-form polymer electrolyte in a sandwiched form between a pair of a positive electrode 2 (2a: electroconductive substrate, 2b: positive composite electrode layer) and a negative electrode 3 (3a: electroconductive substrate, 3b: negative composite electrode layer).

In the case of a lithium ion battery taken

for example, the sheet-form polymer electrolyte 1 may preferably have a thickness of ca. 2 - 1000  $\mu\text{m}$ , particularly ca. 10 - 200  $\mu\text{m}$ , and it is preferred to use a nonaqueous electrolytic solution for

5 impregnation in a proportion of 10 - 1000 wt. parts, particularly 100 - 500 wt. parts, for 100 wt. parts of the vinylidene fluoride copolymer.

Further, in order to provide an improved heat resistance, it is possible to crosslink the polymer electrolyte. As chemical crosslinking means, it is  
10 suitable to apply a vulcanization method for fluoroelastomer obtained by copolymerization of vinylidene fluoride with another monomer. More specifically, the crosslinking may be performed by  
15 adding a polyamine, a polyol or a polyfunctional crosslinking agent, and a radical generating agent.

Suitable examples of the polyamine used for chemical crosslinking may include dibutylamine, piperidine, diethylcyclohexylamine, hexamethylene-  
20 diamine, hexamethylenediamine carbamate, N,N'-dicinnamylidene-1,6-hexanediamine, and 4,4'-bis(aminocyclohexyl) metacarbamate, but these are not restrictive.

Suitable examples of the polyol may include  
25 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)hexafluoropropane, hydroquinone, and 4,4'-dihydroxydiphenylmethane, but these are not

restrictive.

Suitable examples of the polyfunctional crosslinking agent having an unsaturated bond may include: divinylbenzene, ethylene glycol

- 5 dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, propylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, neopentyl glycol
- 10 dimethacrylate, allyl methacrylate, allyl acrylate, 2-hydroxy-1,3-dimethacryloxypropane, bisphenol dimethacrylates, alicyclic dimethacrylates, diacryl isocyanurate, trimethylolpropane trimethacrylate, triacrylformal, triacryl isocyanurate, triallyl
- 15 isocyanurate, aliphatic triacrylates, pentaerythritol tetramethacrylate, pentaerythritol tetraacrylate, and aliphatic tetraacrylates, but these are not restrictive.

- As the radical generator, various organic
- 20 peroxides may be used including, as suitable examples, dialkyl peroxides, such as di-t-butyl peroxide; diacyl peroxides, such as benzoyl peroxide; peroxyketals, such as 2,5-dimethyl-di(t-butylperoxy)hexane; and di-n-peroxydicarbonates, but
- 25 these are not restrictive.

Further, in addition to the above-mentioned polyamine, polyol, polymerizable crosslinking agent

and radical generator, it is also possible to add, as a vulcanization accelerator, a compound which promotes the defluorination of vinylidene fluoride but per se is not readily added. Examples of the vulcanization  
5 accelerator may include organic phosphonium salts and quaternary ammonium salts represented by  $R_4P^+X^-$  and  $R_4N^+X^-$ .

As another method of crosslinking the polymer electrolyte, the irradiation with electron beam or  
10  $\gamma$ -rays may suitably be adopted for introducing the crosslinking structure. The radiation dose in this instance may suitably be on the order of 10 - 500 kGy. In order to enhance the radiation crosslinking effect, it is also suitable to add a polymerizable  
15 crosslinking agent having an unsaturated bond as mentioned above in the solid polymer electrolyte in advance.

The positive electrode 2 and the negative electrode 3 may be obtained by forming a positive  
20 composite electrode layer 2b and a negative composite electrode layer 3b in thicknesses of, e.g., 10 - 1000  $\mu m$  on, e.g., one surface each of electroconductive substrates 2a and 3a comprising a metal foil or metal net comprising iron, stainless steel, copper,  
25 aluminum, nickel, titanium, etc. in thicknesses of 5 - 100  $\mu m$ , e.g., 5 - 20  $\mu m$  in case of small-sized devices.



The positive composite electrode layer 2b and 3b may for example be obtained by applying and drying an electrode-forming slurry composition formed, e.g., by dispersing 1 - 20 wt. parts of powdery electrode materials (positive or negative electrode active substance, and optionally added electroconductivity imparting agent and other additives) in 100 wt. parts of a solution of a vinylidene fluoride copolymer in general inclusive of the above-mentioned vinylidene fluoride copolymer and an electrolytic solution in a volatile organic solvent.

Preferred active substances for lithium ion secondary batteries may include: for positive electrodes, complex metal chalcogenides represented by a general formula of  $\text{LiMY}_2$  (wherein M denotes at least one species of transition metals, such as Co, Ni, Fe, Mn, Cr and V; and Y denotes a chalcogen such as O or S), particularly complex metal oxides as represented by  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  ( $0 \leq x \leq 1$ ) and complex metal oxides having a spinel structure, such as  $\text{LiMn}_2\text{O}_4$ .

Active substances for negative electrodes may include: carbonaceous materials, such as graphite, activated carbon, calcined and carbonized products of phenolic resin and pitch, and coconut shell-based activated carbon, and metal oxides, such as  $\text{GeO}$ ,  $\text{GeO}_2$ ,  $\text{SnO}$ ,  $\text{SnO}_2$ ,  $\text{PbO}$ ,  $\text{PbO}_2$ ,  $\text{SiO}$ ,  $\text{SiO}_2$ , etc., and complex metal oxides of these.

The thus-formed laminated sheet-form battery structure shown in Figure 1 may be, as desired, further laminated as by winding or folding to provide an increased electrode area per unit volume, and  
5 subjected to a treatment, such as enclosure within a relatively simple container and formation of lead electrodes, to provide a non-aqueous battery having an entire structure of, e.g., a rectangle, a cylinder, a coin or a paper-sheet.

10 [Examples]

Hereinbelow, the present invention will be described more specifically with reference to Examples and Comparative Examples.

Incidentally, abnormal linkage contents in  
15 vinylidene fluoride polymers described in Examples below were measured according to the following method.  
[Measurement of abnormal linkage content]

A 20 The abnormal linkage content of a vinylidene fluoride polymer is determined from <sup>19</sup>F-NMR spectrum. <sup>absorption</sup> ~~diffraction~~ peaks

More specifically, ca. 5 mg of a vinylidene fluoride polymer sample is dissolved in a solvent mixture of 0.4 ml of dimethylformamide (DMF) and 0.1 ml of deuterium dimethylformamide (DMF-d<sub>7</sub>) as a  
25 solvent for NMR measurement, and the resultant solution is subjected to the <sup>19</sup>F-NMR measurement at room temperature.

A resultant  $^{19}\text{F}$ -NMR spectrum generally exhibits plural peaks.

Among these peaks, peaks at -113.5 ppm and -115.9 ppm with reference to  $\text{CFCl}_3$  are identified as  
5 peaks attributable to the abnormal linkage.

The abnormal linkage content is determined as follows. The areas of peaks in the range of -90 ppm to -115.9 ppm are respectively measured and summed up to provide a total area  $S_0$ . On the other hand, the  
10 areas of the peaks at -113.5 ppm and -115.9 ppm are denoted by  $S_1$  and  $S_2$ , respectively. Then, the abnormal linkage content is calculated according to the following formula:

$$\begin{aligned} &\text{Abnormal linkage content} \\ 15 \quad &= [(S_1 + S_2) / 2] / S_0 \times 100 (\%) \\ &(\text{Preparation of vinylidene fluoride copolymers}) \\ &(\text{Polymer Preparation Example 1}) \end{aligned}$$

Into an autoclave having an inner volume of 2 liters, 1075 g of deionized water, 0.42 g of methyl  
20 cellulose, 2.9 g of diisopropyl peroxydicarbonate, 378 g of vinylidene fluoride and 42 g of hexafluoropropylene were charged and subjected to 10 hours of suspension polymerization at 29 °C. After completion of the polymerization, the polymerization  
25 slurry was dewatered, washed with water and dried at 80 °C for 20 hours to obtain a polymer powder. The polymerization yield was 89 wt. %, and the resultant

polymer showed an inherent viscosity of 1.7 dl/g. As a result of  $^{19}\text{F}$ -NMR analysis, the polymer exhibited a weight ratio of vinylidene fluoride to

hexafluoropropylene of 93:7, and an abnormal linkage  
5 (head-head or tail-tail linkage) content at vinylidene fluoride sites of 3.6 %.

(Polymer Preparation Example 2)

Into an autoclave having an inner volume of 2 liters, 1036 g of deionized water, 0.40 g of methyl  
10 cellulose, 2.8 g of diisopropyl peroxydicarbonate, 376 g of vinylidene fluoride and 4 g of trichlorofluoroethylene were charged and subjected to 16 hours of suspension polymerization at 28 °C while adding 20 g of trifluorochloroethylene in division of  
15 1 g each at every 30 minutes from 2 hours after the start of the polymerization. After completion of the polymerization, the polymerization slurry was dewatered, washed with water and dried at 80 °C for 20 hours to obtain a polymer powder. The polymerization  
20 yield was 86 wt. %, and the resultant polymer showed an inherent viscosity of 1.8 dl/g. As a result of  $^{19}\text{F}$ -NMR analysis, the polymer exhibited a weight ratio of vinylidene fluoride to trifluorochloroethylene of 95:5.

25 (Polymer Preparation Example 3)

Into an autoclave having an inner volume of 2 liters, 1075 g of deionized water, 0.42 g of methyl

cellulose, 2.9 g of diisopropyl peroxydicarbonate, 365 g of vinylidene fluoride, 30 g of hexafluoropropylene and 25 g of trifluorochloroethylene were charged and subjected to 11 hours of suspension polymerization at 29 °C. After completion of the polymerization, the polymerization slurry was dewatered, washed with water and dried at 80 °C for 20 hours to obtain a polymer powder. The polymerization yield was 90 wt. %, and the resultant polymer showed an inherent viscosity of 1.8 dl/g. As a result of <sup>19</sup>F-NMR analysis, the polymer exhibited weight ratios of vinylidene fluoride to hexafluoropropylene to trifluorochloroethylene of 90:5:5.

(Polymer Preparation Example 4)

Into an autoclave having an inner volume of 2 liters, 1140 g of deionized water, 0.29 g of methyl cellulose, 4.4 g of diisopropyl peroxydicarbonate, 326 g of vinylidene fluoride and 52 g of hexafluoropropylene were charged and subjected to 11 hours of suspension polymerization at 29 °C while adding 204 g of vinylidene fluoride in division of 17 g each at every 25 minutes from 3 hours after the start of the polymerization. After completion of the polymerization, the polymerization slurry was dewatered, washed with water and dried at 80 °C for 20 hours to obtain a polymer powder. The polymerization yield was 90 wt. %, and the resultant polymer showed

an inherent viscosity of 1.7 dl/g. As a result of  $^{19}\text{F}$ -NMR analysis, the polymer exhibited a weight ratio of vinylidene fluoride to hexafluoropropylene of 93:7. (Polymer Preparation Example 5)

5           Into an autoclave having an inner volume of 2 liters, 1075 g of deionized water, 0.21 g of methyl cellulose, 2.9 g of diisopropyl peroxydicarbonate, 378 g of vinylidene fluoride and 42 g of hexafluoropropylene were charged and subjected to  
10 suspension polymerization at 29 °C for 6 hours. When the pressure was lowered by 0.3 MPa from the pressure at the start of the polymerization, the temperature was raised to 40 °C, and polymerization was performed for further 6 hours. After completion of the  
15 polymerization, the polymerization slurry was dewatered, washed with water and dried at 80 °C for 20 hours to obtain a polymer powder. The polymerization yield was 84 wt. %, and the resultant polymer showed an inherent viscosity of 1.7 dl/g. As a result of  
20  $^{19}\text{F}$ -NMR analysis, the polymer exhibited a weight ratio of vinylidene fluoride to hexafluoropropylene of 93:7, and an abnormal linkage content at vinylidene fluoride sites of 4.0 %.

(Polymer Preparation Example 6)

25           Into an autoclave having an inner volume of 2 liters, 1075 g of deionized water, 0.21 g of methyl cellulose, 2.9 g of diisopropyl peroxydicarbonate, 370

g of vinylidene fluoride and 50 g of  
hexafluoropropylene were charged and subjected to 18  
hours of suspension polymerization at 29 °C. After  
completion of the polymerization, the polymerization  
5 slurry was dewatered, washed with water and dried at  
80 °C for 20 hours to obtain a polymer powder. The  
polymerization yield was 89 wt. %, and the resultant  
polymer showed an inherent viscosity of 1.9 dl/g. As  
a result of <sup>19</sup>F-NMR analysis, the polymer exhibited a  
10 weight ratio of vinylidene fluoride to  
hexafluoropropylene of 91:9.

(Polymer Preparation Example 7)

Into an autoclave having an inner volume of 2  
liters, 1075 g of deionized water, 0.21 g of methyl  
15 cellulose, 2.1 g of diisopropyl peroxydicarbonate, 378  
g of vinylidene fluoride and 42 g of  
hexafluoropropylene were charged and subjected to 8  
hours of suspension polymerization at 29 °C. After  
completion of the polymerization, the polymerization  
20 slurry was dewatered, washed with water and dried at  
80 °C for 20 hours to obtain a polymer powder. The  
polymerization yield was 88 wt. %, and the resultant  
polymer showed an inherent viscosity of 2.5 dl/g. As  
a result of <sup>19</sup>F-NMR analysis, the polymer exhibited a  
25 weight ratio of vinylidene fluoride to  
hexafluoropropylene of 93:7.

(Example 1)

10 g of the polymer obtained in Polymer Preparation Example 1 and 100 g of a mixture solution of ethylene carbonate, propylene carbonate and tetrahydrofuran (in mixing weight ratios of 15:15:70) were blended to form a solution. The solution was cast, and the tetrahydrofuran was removed therefrom by air drying to form a ca. 80  $\mu$ m-thick gel-form film containing the ethylene carbonate and propylene carbonate at ca. 75 wt. %. (As a result of weighing of the resultant gel-form film, a weight loss corresponding to the used tetrahydrofuran was confirmed.)

According to ASTM D882, a test piece was cut out from the gel-form film in a test length of 20 mm and a test width of 10 mm and subjected to measurement of a tensile strength at a tensile speed of 100 mm/min. by using TENSILON UTM-III-100 (made by TOYO BALDWIN K.K.), whereby a value of 2.54 MPa was obtained.

(Example 2)

A ca. 100  $\mu$ m-thick gel-form film containing ca. 75 wt. % of ethylene carbonate and propylene carbonate was obtained in the same manner as in Example 1 except for using the polymer obtained in Polymer Preparation Example 2. As a result of weighing of the gel-form film, a weight loss corresponding to the used tetrahydrofuran was



confirmed.

As a result of a tensile strength measurement of the gel-form film in the same manner as in Example 1, a value of 2.01 MPa was obtained.

5 (Example 3)

A ca. 100  $\mu$ m-thick gel-form film containing ca. 75 wt. % of ethylene carbonate and propylene carbonate was obtained in the same manner as in Example 1 except for using the polymer obtained in  
10 Polymer Preparation Example 3. As a result of weighing of the gel-form film, a weight loss corresponding to the used tetrahydrofuran was confirmed.

As a result of a tensile strength measurement  
15 of the gel-form film in the same manner as in Example 1, a value of 1.54 MPa was obtained.

(Comparative Example 1)

A ca. 100  $\mu$ m-thick gel-form film containing ca. 75 wt. % of ethylene carbonate and propylene  
20 carbonate was obtained in the same manner as in Example 1 except for using as the polymer "KYNAR 2801" (more specifically "Kynar FLEX 2801" made by Atochem Co., a vinylidene fluoride/hexafluoropropylene copolymer; a vinylidene fluoride/hexafluoropropylene  
25 nominal weight ratio = 88/12. According to the inventors' measurement, vinylidene fluoride/hexafluoropropylene weight ratio = 90/10

based on NMR analysis and inherent viscosity = 1.2 dl/g). As a result of weighing of the gel-form film, a weight loss corresponding to the used tetrahydrofuran was confirmed.

5           As a result of a tensile strength measurement of the gel-form film in the same manner as in Example 1, only a weak strength of 0.76 MPa was obtained. (Example 4)

10           In a nitrogen atmosphere having a dew point of below  $-70^{\circ}\text{C}$ , 10 g of the polymer obtained in Polymer Preparation Example 1 and 5 g of  $\text{LiPF}_6$  were blended with 100 g of a solution mixture of ethylene carbonate, propylene carbonate and tetrahydrofuran (in mixing wt. ratios of 15:15:70) to form a solution.

15   The solution was cast, and the tetrahydrofuran was removed by air drying to form a ca. 80  $\mu\text{m}$ -thick gel-form polymer electrolyte film. As a result of weighing of the resultant gel-form polymer electrolyte film, a weight loss corresponding to the used

20   tetrahydrofuran was confirmed.

          The gel-form polymer electrolyte exhibited little exudation of the electrolytic solution and was found to be soft, stretchable and strong as a result of pulling by hands. A test piece of 50 mm x 50 mm

25   was cut out from the gel-form polymer electrolyte film and, after weighing, stored for 2 weeks at  $-18^{\circ}\text{C}$ , followed by restoration to room temperature, light

wiping of the film surface to remove the electrolytic solution at the film surface and weighing to determine a percentage weight loss due to exudation for evaluating the electrolytic solution-retentivity.

- 5 Herein, the percentage weight loss is given by  
((weight before storage - weight after  
storage)/(weight before storage)) x 100, and a smaller  
value indicates a stabler electrolytic solution-  
retentivity with time. The percentage weight loss was  
10 a small value of 0.38 %, thus indicating an excellent  
electrolytic solution-retentivity.

(Example 5)

- A 15 A ca. 80  $\mu$ m-thick gel-form polymer  
electrolyte film was prepared in the same manner as in  
Example <sup>4</sup>~~5~~ except for using the polymer prepared in  
Polymer Preparation Example 2. As a result of  
evaluation of electrolytic solution-retentivity of the  
gel film in the same manner as in Example 4, the  
percentage weight loss due to exudation was as small  
20 as 0.11 %, thus indicating an excellent electrolytic  
solution-retentivity.

(Example 6)

- A 25 A ca. 80  $\mu$ m-thick gel-form polymer  
electrolyte film was prepared in the same manner as in  
Example <sup>4</sup>~~5~~ except for using the polymer prepared in  
Polymer Preparation Example 3. As a result of  
evaluation of electrolytic solution-retentivity of the

gel film in the same manner as in Example 4, the percentage weight loss due to exudation was as small as 0.49 %, thus indicating an excellent electrolytic solution-retentivity.

5 (Comparative Example 2)

A ca. 80  $\mu$ m-thick gel-form polymer electrolyte film was prepared in the same manner as in Example 4 except for using as the polymer "KYNAR 2801" (vinylidene fluoride/hexafluoropropylene weight ratio  
10 = 88/12, inherent viscosity 1.2 dl/g). As a result of weighing of the resultant gel-form polymer electrolyte film, a weight loss corresponding to the used tetrahydrofuran was confirmed.

The gel-form polymer electrolyte film  
15 exhibited exudation of the electrolytic solution and a clearly inferior strength than those of ~~Examples 3 and 4~~ <sup>Examples 4 and 5</sup> and  
A ~~4~~ Further, as a result of evaluation of electrolytic solution-retentivity in the same manner as in Example  
A 4, the percentage weight loss due to exudation was as  
20 large as 1.50 %, thus indicating an inferior electrolytic solution-retentivity.

(Example 7)

10 g of the polymer obtained in Polymer Preparation Example 3 was dissolved in 90 g of  
25 tetrahydrofuran, and 0.5 g of hexamethylenediamine as a crosslinking agent and 0.5 g of carbon black as an accelerator were added thereto to prepare a first

solution. Then, 4.5 g of  $\text{LiPF}_6$  was dissolved in 3 ml of a mixture solution of propylene carbonate and ethylene carbonate in a volume ratio of 1:1 to prepare a second solution. The first solution and the second  
5 solution were blended and well stirred for 12 hours at  $50^\circ\text{C}$ , followed by casting onto a glass sheet and removal of the tetrahydrofuran by air drying to obtain a gel-form polymer electrolyte film. As a result of weighing of the resultant ca. 80  $\mu\text{m}$ -thick gel film, a  
10 weight loss corresponding to the used tetrahydrofuran was confirmed.

As a result of tensile strength measurement of the gel-form film in the same manner as in Example 1, a value of 3.61 MPa was obtained.

15 Then, as a heat resistance test, the gel-form film was hermetically sealed up in a glass bottle and heated for 1 hour within an oven at  $100^\circ\text{C}$ , followed by taking out and cooling to room temperature. The gel-form film after the cooling retained its original  
20 shape without melting during the heating.

(Example 8)

In a nitrogen atmosphere having a dew point of below  $-70^\circ\text{C}$ , 10 g of the polymer prepared in Polymer Preparation Example 1 and 5 g of  $\text{LiPF}_6$  were  
25 dissolved in 100 g of a mixture solution of propylene carbonate, ethylene carbonate and dimethyl carbonate (in mixing wt. ratios of 15:15:70) to form a first

solution. On the other hand, 7 g of polyvinylidene fluoride ("KF#1300", made by Kureha Kagaku K.K.; inherent viscosity = 1.30 dl/g) was mixed with 85 g of LiCoO<sub>2</sub>, 8 g of electroconductive carbon black and 60 g of N-methyl-2-pyrrolidone, and the resultant slurry was applied on a 10 μm-thick aluminum foil, followed by vaporization removal of the N-methyl-2-pyrrolidone to form a ca. 110 μm-thick dry electrode (positive electrode). Further, 10 g of polyvinylidene fluoride ("#9100", made by Kureha Kagaku K.K.; inherent viscosity = 1.10 dl/g) was mixed with 90 g of a pitch-based porous carbonaceous material and 90 g of N-methyl-2-pyrrolidone, and the resultant slurry was applied onto a 10 μm-thick copper foil, followed by vaporization removal of the N-methyl-2-pyrrolidone to form a ca. 105 μm-thick dry electrode (negative electrode).

Then, the first solution was divided into equal halves which were then separately applied onto the active substances of the positive electrode and the negative electrode, followed by air drying to cause evaporation-off of ca. 60 g of the dimethyl carbonate having a lower boiling point and form a gel-form polymer electrolyte layer on the positive and negative electrodes. The positive electrode and the negative electrode each coated with the gel layer were laminated with their gel layers inside by a double

roller laminator, thereby forming a paper-form battery having a total thickness of ca. 0.7 mm including a battery case.

The paper-form battery was bent at 90 deg.

5 and, in the bent state, subjected to a charging operation according to a constant current-constant voltage charging method wherein the battery was first charged at a current density of  $1.8 \text{ mA/cm}^2$  up to a battery voltage of 4.2 volts and then held at a  
10 constant voltage of 4.2 volts within a total changing time not exceeding 3.5 hours, followed by a discharging operation according to a constant current discharging method wherein the battery was discharged at a current density of  $1.8 \text{ mA/cm}^2$  down to a final  
15 voltage of 2.5 volts. In the first cycle, the battery exhibited a charging capacity of 332 mAh/g (carbon material) and a discharge capacity of 287 mAh/g (carbon material). On further repetition of the charge-discharge cycles, the discharge capacity at  
20 20th-cycle was 97 % of the capacity at the first cycle. During the cycles, the charge-discharge operations were smoothly performed without causing liquid leakage.

(Comparative Example 3)

25 A paper-form battery was prepared in the same manner as in Example 8 except for using as the polymer "KYNAR 2801" (vinylidene fluoride/hexafluoro-

propylene weight ratio = 88/12, inherent viscosity = 1.2). The same charge-discharge test in a bent state at 90 deg. as in Example 8 was tried to be applied to the battery, whereas a short circuit between the positive and negative electrodes was caused presumably due to breakage of the gel electrolyte layer so that the charging was failed.

(Example 9)

A ca. 100  $\mu$ m-thick gel-form film containing ca. 75 wt. % of ethylene carbonate and propylene carbonate was prepared in the same manner as in Example 1 except for using the polymer obtained in Polymer Preparation Example 4. As a result of weighing of the gel-form film, a weight was corresponding to the used tetrahydrofuran was confirmed. As a result of a tensile strength measurement of the gel-form film, a value of 1.68 MPa was obtained.

A ca. 80  $\mu$ m-thick gel-form polymer electrolyte film was prepared in the same manner as in Example 4 except for using the polymer obtained in Polymer Preparation Example 4. As a result of evaluation of electrolytic solution-retentivity of the gel film in the same manner as in Example 4, the percentage weight loss due to exudation was at a small value of 0.53 %, thus exhibiting an excellent electrolytic solution-retentivity.



The above Examples are comparable to Examples 1 and 4 in respects of polymer composition and inherent viscosity. Thus, it is understood that the polymer of Polymer Preparation Example 1 obtained by polymerization of the monomers charged simultaneously provided higher strength and higher electrolytic solution-retentivity than the polymer of Polymer Preparation example 4 obtained by polymerization of the monomers charged in division.

10 (Example 10)

A ca. 100  $\mu\text{m}$ -thick gel-form film containing ca. 75 wt. % of ethylene carbonate and propylene carbonate was prepared in the same manner as in Example 1 except for using the polymer obtained in Polymer Preparation Example 5. As a result of weighing of the gel-form film, a weight was corresponding to the used tetrahydrofuran was confirmed. As a result of a tensile strength measurement of the gel-form film, a value of 2.22 MPa was obtained.

A ca. 80  $\mu\text{m}$ -thick gel-form polymer electrolyte film was prepared in the same manner as in Example 4 except for using the polymer obtained in Polymer Preparation Example 5. As a result of evaluation of electrolytic solution-retentivity of the gel film in the same manner as in Example 4, the percentage weight loss due to exudation was as small

as 0.13 %, thus exhibiting an excellent electrolytic solution-retentivity.

The above Examples are comparable to Examples 1 and 4 in respects of polymer composition and inherent viscosity. Thus, it is understood that the polymer of Polymer Preparation Example 5 obtained through a higher polymerization temperature provided a higher electrolytic solution-retentivity than the polymer of Polymer Preparation example 1 obtained at a lower polymerization temperature. This may be understood as a result of an increased abnormal linkage content owing to an elevated polymerization temperature.

(Example 11)

A ca. 100  $\mu$ m-thick gel-form film containing ca. 75 wt. % of ethylene carbonate and propylene carbonate was prepared in the same manner as in Example 1 except for using the polymer obtained in Polymer Preparation Example 6. As a result of weighing of the gel-form film, a weight was corresponding to the used tetrahydrofuran was confirmed. As a result of a tensile strength measurement of the gel-form film, a value of 1.45 MPa was obtained.

A ca. 80  $\mu$ m-thick gel-form polymer electrolyte film was prepared in the same manner as in Example 4 except for using the polymer obtained in

Polymer Preparation Example 6. As a result of evaluation of electrolytic solution-retentivity of the gel film in the same manner as in Example 4, the percentage weight loss due to exudation was as small  
5 as 0.10 %, thus exhibiting an excellent electrolytic solution-retentivity.

(Example 12)

A ca. 100  $\mu\text{m}$ -thick gel-form film containing ca. 75 wt. % of ethylene carbonate and propylene  
10 carbonate was prepared in the same manner as in Example 1 except for using the polymer obtained in Polymer Preparation Example 7. As a result of weighing of the gel-form film, a weight was corresponding to the used tetrahydrofuran was  
15 confirmed. As a result of a tensile strength measurement of the gel-form film, a value of 2.76 MPa was obtained.

A ca. 80  $\mu\text{m}$ -thick gel-form polymer electrolyte film was prepared in the same manner as in  
20 Example 4 except for using the polymer obtained in Polymer Preparation Example 7. As a result of evaluation of electrolytic solution-retentivity of the gel film in the same manner as in Example 4, the percentage weight loss due to exudation was as small  
25 as 0.07 %, thus exhibiting an excellent electrolytic solution-retentivity.

[INDUSTRIAL APPLICABILITY]

As is clear from the above Examples and Comparative Examples, according to the present invention, it is possible to obtain a polymer electrolyte present in a state of containing much nonaqueous electrolytic solution and exhibiting an excellent strength in this state by using a vinylidene fluoride copolymer having a high vinylidene fluoride content and a high inherent viscosity. Further, by using the polymer electrolyte, it is possible to obtain a nonaqueous battery having stable strength and properties and also a high shape latitude.

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